

## THE SENSITIVITY OF TROPOSPHERIC CHEMISTRY TO CLOUD INTERACTIONS.

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## ABSTRACT

Clouds, although only occupying a relatively small fraction of the tropospheric volume can have a substantial impact on the chemistry of the troposphere. In newly formed clouds, or in clouds with air rapidly flowing through, the chemistry is expected to be far more active than in aged clouds with stagnant air. Thus frequent cycling of air through shortlived clouds, i.e. cumulus clouds, is likely to be a much more efficient media for altering the composition of the atmosphere than an extensive cloud cover i.e. frontal cloud systems.

The impact of clouds is tested out in a 2-D channel model encircling the globe in a latitudinal belt from 30 to 60°N. The model contains a detailed gas phase chemistry. In addition physiochemical interactions between the gas and aqueous phases are included. For species as  $\text{H}_2\text{O}_2$ ,  $\text{CH}_2\text{O}$ ,  $\text{O}_3$  and  $\text{SO}_2$ , Henry's law equilibria are assumed, whereas  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  are regarded as completely dissolved in the aqueous phase. Absorption of  $\text{HO}_2$  and  $\text{OH}$  is assumed to be mass-transport limited.

The chemistry of the aqueous phase is characterized by rapid cycling of odd hydrogen ( $\text{H}_2\text{O}_2$ ,  $\text{HO}_2$  and  $\text{OH}$ ).  $\text{O}_2^-$  (produced through dissociation of  $\text{HO}_2$ ) reacting with dissolved  $\text{O}_3$  is a major source of  $\text{OH}$  in the aqueous phase. This reaction can be a significant sink for  $\text{O}_3$  in the troposphere. In the interstitial cloud air, odd hydrogen is depleted, whereas  $\text{NO}_x$  remains in the gas phase, thus reducing ozone production due to the reaction between  $\text{NO}$  and  $\text{HO}_2$ . Our calculations give markedly lower ozone levels when cloud interactions are included. This may in part explain the overpredictions of ozone levels often experienced in models neglecting cloud chemical interactions.

In the present study the existence of clouds, cloud types and their lifetimes are modelled as pseudo random variables. Such pseudo random sequences are in reality deterministic and may, given the same starting values, be reproduced. The effects of cloud interactions on the overall chemistry of the troposphere will be discussed. In particular, tests are performed to determine the sensitivity of cloud frequencies and cloud types.

## 1. INTRODUCTION.

Measurements indicates that since the turn of the century there has been a marked increase in tropospheric ozone levels particularly over northern mid latitudes (Bojkov, 1986; Kley et al., 1988). The increase is a result of man made emissions of hydrocarbons and  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) compounds (Crutzen, 1988). Tropospheric ozone is an active greenhouse gas, and thus increased ozone levels, particularly in the Northern Hemisphere could contribute to global warming.

Several past model studies of tropospheric ozone have had a tendency to overpredict ozone (i.e. Isaksen et al., 1989; Jonson and Isaksen, 1992a). Lelieveld and Crutzen (1990, 1991) proposed that clouds may act as an efficient sink for ozone, predominantly through the aqueous phase reaction with  $\text{O}_2^-$ . In fact, they found this reaction to be so fast that without a fixed ozone value, ozone levels would have become unrealistically low. Jonson and Isaksen (1992b) calculate a much smaller, but nonetheless, significant impact of clouds on ozone levels. They found that about half of the ozone reductions could be attributed to indirect effects on the gas phase chemistry, the other half to the aqueous phase reaction with  $\text{O}_2^-$ .

Lelieveld and Crutzen (1990, 1991) and Jonson and Isaksen (1992b) used crude parameterizations for clouds. Lelieveld and Crutzen (1990, 1991) assumed average cycling times in and out of clouds based on lagrangian statistics. Jonson and Isaksen (1992b) assumed stationary clouds with the air flowing through. The present study applies the same model, but a more flexible cloud parameterization is used. Based on statistics for the fractional cloud cover, clouds are distributed according to a pseudo random function.

Several species will reach concentrations in the aqueous phase several orders of magnitude higher than in the gas phase. Provided fast aqueous phase reactions occur, several soluble species are rapidly removed in clouds. Thus, important aqueous phase processes are likely to become far less important with increasing residence time for air in clouds.

## 2. DESCRIPTION.

The model covers the latitudinal belt from 30 - 60°N. The horizontal resolution is 10° longitude and the vertical resolution 500 m from ground level to 3 km and 1 km from 3 to 16 km, the upper boundary of the model. The timestep is 1 hour, and the model is run for 30 days. Mid-april conditions are simulated. The zonal distributions of both natural and anthropogenic emissions of NO<sub>x</sub> (NO+NO<sub>2</sub>), non-methane hydrocarbons and CO are taken from Isaksen et al. (1989), while emissions of SO<sub>2</sub> are from Jonson and Isaksen (1992a). For the advection, seasonally averaged wind fields are used (Oort, 1983). The advection equation is solved by an upwind scheme with corrections for numerical dispersion (Smolarkiewicz, 1983). In the vertical, the eddy diffusion is separated into a slow diffusive transport, and a rapid cloud transport. The cloud transport is a combination of direct transport from cloud base to any layer between cloud base and cloud top, and a slower compensating subsidence to the layer below. This method was first described by Chatfield and Crutzen (1984). Cloud transport takes place at every longitude, regardless of whether cloudy or cloud free conditions, as described below, are assumed. However, in clouds, the cloud transport is multiplied by 1.6, outside clouds by 0.2, emphasizing cloud advection where the bulk of the clouds are assumed to be concentrated. The advection, eddy diffusion and cloud transport are described in more detail by Solberg (1989).

Whether a grid rectangle will be in clouds (cloud mode) or not is determined by a pseudo random function. Each grid rectangle is assigned a probability for cloud based on statistics for the fractional cloud cover (Gordon et al., 1984). Whenever the cloud mode is selected by the random function, the model has a choice of 4 cloud categories. Each cloud category is assigned a probability and a corresponding residence time. Probabilities for the 4 cloud categories, their residence times and their height intervals and optical thickness are listed in Table 1. If a clear sky situation is selected, a choice is made between 4 residence times. The probability for a residence time of 31 hours is 0.1, a residence time of 6 hours, 0.2, a residence time of 2 hours, 0.4, and of 1 hour, 0.3. The overall probability for the individual cloud categories and for the length of the clear sky periods are determined by the product of the probabilities and their residence times. When selected the average residence times for clear sky and cloud events are equal. The overall probabilities for clouds are thus determined by the cloud fractions. This pseudo random sequence can be reproduced given the same starting values. Different sets of dissociation rates are calculated for the 4 cloud categories and for clear sky conditions (Jonson and Isaksen, 1992b).

The chemistry (gas- and aqueous- phase) has been described by Jonson and Isaksen (1992b). In clouds, we assume that H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> are completely absorbed by the droplets. For H<sub>2</sub>O<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, HCHO and HCOOH, equilibrium between the gas- and liquid- phase, determined by Henry's law constants and equilibrium constants, are

applied. The fraction of the total (gas and liquid) concentration dissolved in the aqueous phase is defined as

$$f = \frac{1}{1 + (LH_{eff}RT)^{-1}}$$

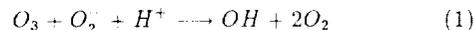
where L is the volume ratio between gas and liquid water, H<sub>eff</sub> is the efficient Henry's constant (taking into account the effect of dissociation), R is the universal gas constant and T the temperature. In clouds, the aqueous phase concentration is then calculated as f multiplied by the total (gas and liquid) concentration, and the gas phase concentration as (1-f) multiplied by the total concentration. The mass-transfer of OH and HO<sub>2</sub> is assumed to be mass-transport limited, and is calculated as described by Schwartz (1986). In the previous study (Jonson and Isak-

Cat.	Prob.	Res.	Height (km)	Opt.
1	0.1	3	0 - 0.5	see caption
2	0.2	10	7 - 8(9) 5 - 7 0.5(2) - 4	5 15 20
3	0.2	8	2.5 - 5	30
4	0.5	3	0.5(2)-6(7)	30

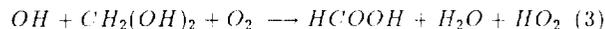
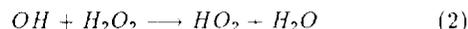
Table 1: When cloud mode is selected, Prob. denotes the probability for a cloud category, Res. the residence time in hours of the cloud event, Height, denotes the height interval(s) for the cloud layer(s) and Opt., the optical thickness of the cloud. For category 1, J-values for clear sky are multiplied by a factor 1.5 in the lowest layer. Numbers in brackets denote cloud-base and cloud-top heights over land.

sen, 1992b), we showed that aqueous phase chemistry has a substantial impact on the composition of the gas phase. The processes were studied with clouds fixed in space and time. This simple approach has the advantage of providing stable conditions where the individual reactions can be studied in more detail. Two processes, resulting in reduced ozone levels compared to gas-phase chemistry only, were identified:

The first process is the aqueous phase loss through the reaction:



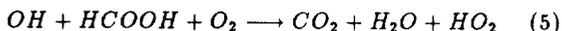
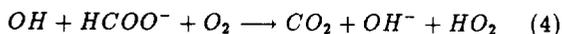
Although ozone has a low solubility in water, the reaction is nonetheless a significant sink for ozone. This reaction is also a major source of OH in the aqueous phase. The sources of O<sub>2</sub> ⇌ HO<sub>2</sub> are absorption from the gas phase and recycling of hydrogen from OH through the aqueous phase reactions:



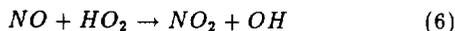
Long.	short cycling				long cycling			
	fc	P	$Q_g$	$Q_{aq}$	fc	P	$Q_g$	$Q_{aq}$
150°W	0.63	1.8E+6	1.1E-6	7.5E-7	0.7	2.0E+6	1.2E-6	6.2E-7
80°W	0.74	6.8E+6	5.0E-7	2.3E-7	0.69	6.5E+6	5.4E-7	2.2E-7
30°W	0.7	2.5E+6	1.4E-7	3.3E-7	0.72	2.4E+6	1.5E-6	2.4E-7
20°E	0.48	6.8E+6	5.0E-7	2.1E-7	0.41	6.7E+6	6.0E-7	2.1E-7
mean	0.38	4.3E+6	8.7E-7	4.4E-7	0.39	4.7E+6	9.9E-7	3.4E-7

Table 2: Ozone production and loss terms for selected longitudes and mean values for the whole model volume.  $fc$  is the fractional time in the cloud mode.  $P$  is the production of ozone in molecules  $cm^{-3}s^{-1}$ , and  $Q_g$  and  $Q_{aq}$  the gas- and aqueous- phase loss of ozone in  $s^{-1}$  averaged over a 30 day period for the lowest 6750 meters of the troposphere.

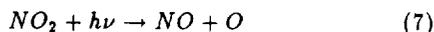
Formic acid partially evaporates, but it also contributes to the cycling of hydrogen:



The second process which leads to reduced ozone levels is due to reduced gas phase production through the reaction sequence:



In sunlight  $NO_2$  is photolyzed:



$O$  rapidly combines with  $O_2$  giving ozone. Whereas most of the odd hydrogen ( $OH$ ,  $HO_2$  and  $H_2O_2$ ), and thereby  $HO_2$ , resides in the aqueous phase,  $NO_x$  has a low solubility, and will remain in the gas phase. The effect is reduced ozone production.

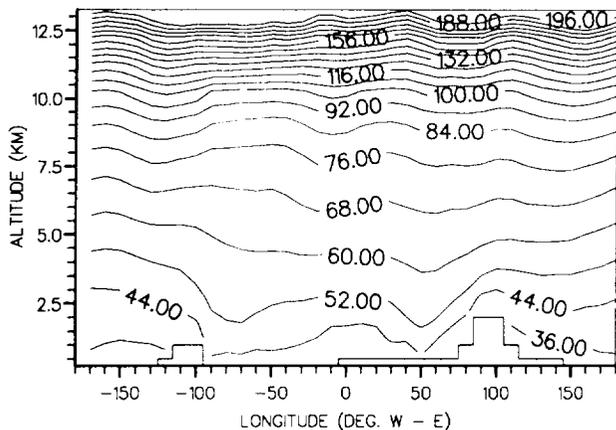


Figure 1: Diurnally averaged ozone concentrations for the Northern mid- latitudes as a function of latitude and altitude. Concentrations are given in parts per billion (ppb).

In the gas phase, ozone is destroyed by a number of species, including  $HO_2$ .

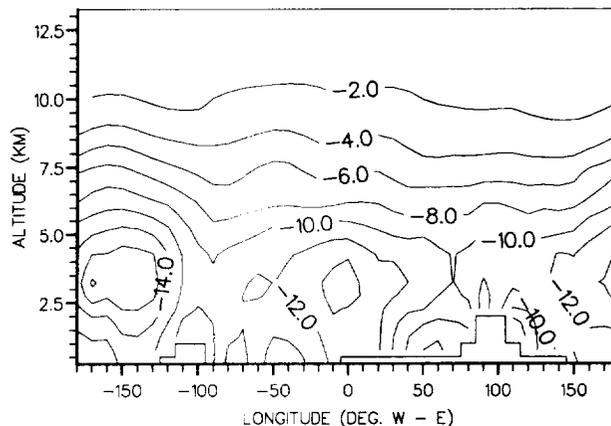
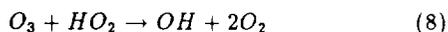


Figure 2: Percentage difference in ozone concentrations between model runs without cloud chemistry and with cloud chemistry as a function of longitude and altitude.

### 3. COMPUTATIONAL RESULTS.

In this study we are interested in quantifying the effects of different cloud representations rather than to study the individual reactions in detail. In Figure 1 ozone concentrations are shown with random clouds as described above. Figure 2 shows the percentage difference between concentrations calculated with no cloud chemistry (but with identical dissociation rates) and calculations with cloud chemistry. With cloud chemistry included, concentrations are lower throughout the troposphere. Ozone produced over polluted continents (North America, Europe and East Asia) is transported eastwards. During transport ozone is destroyed in clouds. In particular, large differences are found at the eastern rim of the Atlantic and Pacific oceans, downwind from North America and East Asia respectively.

Figure 3 shows the percentage difference in ozone concentrations between a model run with residence times doubled, and a run where residence times have been approximately halved. Effects on ozone are generally small, and are slightly negative over polluted continents, most likely due to changes in the  $NO_x$  distribution. In Table 2, ozone production and loss rates are shown. The tabulated values are averages for the whole period studied, with both cloudy and cloud free periods included. The effect of long and

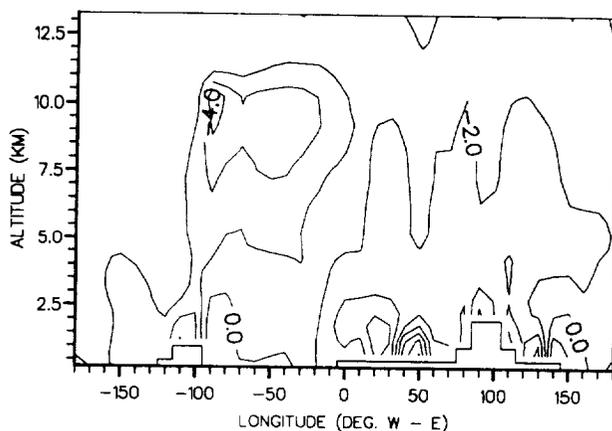


Figure 1: Percentage difference in ozone concentrations between model runs with long and short residence times for clouds.

short cloud cycling times are compared. Production rates (reaction 6) and loss rates for ozone reacting with  $\text{HO}_2$  in both gas and aqueous phase (reaction 8 and 2 respectively) are tabulated. Over the polluted continents ( $80^\circ\text{W}$  and  $20^\circ\text{E}$ ) production rates are about a factor of 10 higher than over remote oceanic sites ( $150^\circ\text{W}$  and  $30^\circ\text{W}$ ). With short residence times the aqueous phase loss (reaction 2) is about 30% higher averaged over the whole model volume. This is compensated for by lower loss rates in the gas phase (reaction 8). However, Figure 3 show that ozone concentrations generally are lower in calculations with short cloud cycling times. These changes are caused by indirect effects on the  $\text{NO}_x$  chemistry and distribution rather than changes in aqueous phase destruction.

#### 4. CONCLUSIONS.

Aqueous phase chemistry can reduce ozone concentrations in the troposphere significantly. Two mechanisms are identified by which ozone is reduced. Ozone absorbed in the droplets are consumed by a reaction with  $\text{O}_2^-$ . Secondly  $\text{HO}_2$  and  $\text{NO}$  are separated in the clouds, as  $\text{HO}_2$  is absorbed by the droplets whereas  $\text{NO}$  is virtually insoluble, thus slowing ozone production. Variations in residence times for cloud events does not alter the ozone concentrations by more than a few percent. With such a low sensitivity to cloud cycling parameterization, it is justified to apply the proposed mechanism even in models with low resolution where individual clouds, or even entire cloud systems are not properly resolved.

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#### 5. REFERENCES.

- Bojkov R.D.** (1986) Surface ozone during the second half of the nineteenth century. *J. Chem. Appl. Meteor.*, Vol. 25, pp 343-352.
- Chatfield R.B. and Crutzen P.** (1984) Sulfur dioxide in remote oceanic air. Cloud transport of reactive precursors. *J. Geophys. Res.*, Vol. 89, pp 7111-7132.
- Crutzen P.J.** (1988) Tropospheric ozone: an overview. *Tropospheric Ozone - Regional and Global Scale Interactions*, edited by I.S.A. Isaksen. NATO ASI Series c, D Reidel, Dordrecht, The Netherlands, Vol. 227, pp 3-33.
- Gordon C.T., Hovanec R.D., Stern W.F.** (1984) Analyses of monthly mean cloudiness and their influence upon model-diagnosed radiative fluxes. *J. Geophys. Res.*, Vol. 89, pp 4713-4738.
- Isaksen I.S.A., Jonson J.E., Reeves C.E., Solberg S., Chatfield R.** (1989) Model studies of free tropospheric ozone formation from pollution sources. *Proceedings of the 4'th Quadrennial Ozone Symposium*. Ed. by R. D. Bojkov and P. Fabian A. DEPAK Publishing, pp 544-548.
- Jonson J.E., Isaksen I.S.A.** (1992) Parameterization of episodic cloud and rainout events in large-scale atmospheric chemistry models. *Atmospheric Environment*. Vol. 26A, No. 11, pp. 2019-2029.
- Jonson J.E., Isaksen I.S.A.** (1992) Tropospheric ozone chemistry: The impact of cloud chemistry. Accepted by *J. Atm. Chem.*
- Kley D., Volz A., Mulheims F.** (1988) Ozone measurements in historic perspective, *Tropospheric Ozone - Regional and Global Scale Interactions*, edited by I.S.A. Isaksen. NATO ASI Series c, D Reidel, Dordrecht, The Netherlands, Vol. 227, pp 63-72.
- Lelieveld J. and Crutzen P.J.** (1990) Influences of cloud photochemical processes on tropospheric ozone. *Nature*, Vol. 343, pp. 227-233.
- Lelieveld J. and Crutzen P.J.** (1991) The role of clouds in tropospheric photochemistry. *J. of Atm. Chem.* Vol. 12, pp 229-267.
- Oort A.H.** (1983) Global atmospheric circulation statistics, 1958 - 1973, *NOAA professional paper 14*.
- Schwartz S.E.** (1986) Mass-transport considerations pertinent to aqueous phase reactions of gases in liquid-water clouds. *Chemistry of multiphase atmospheric systems*. Ed. by W. Jaeschke, Springer-Verlag, Berlin, pp 415-471.
- Smolarkiewicz P.K.** (1983) A simple positive definite advection scheme with small implicit diffusion. *Monthly Weather Rev.*, Vol 111, pp 476-487.
- Solberg S., Isaksen I.S.A., Chatfield R.** (1989) Design of a channel model to assess mid-latitude pollution effects. *Proceedings of the 4'th Quadrennial Ozone Symposium*. Ed. by R.D. Bojkov and P. Fabian A. DEPAK Publishing, pp 548-552.